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(54) TRANSPARENT CONDUCTIVE BASE MATERIAL, ITS MANUFACTURE AND DISPLAY
DEVICE USING THIS BASE MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a transparent conductive base material that is excellent in weather resistance, conductivity and the like and allows its manufacturing cost to be reduced, and provide its manufacturing method, and also provide a display device to which this transparent conductive base material is applied.

SOLUTION: This transparent conductive base material is based on a transparent conductive base material equipped with a transparent double layer film composed of a transparent board, and a transparent conductive layer and a transparent coating layer which are formed on the transparent board sequentially; the transparent conductive layer is formed by using noble metal-coated fine silver particles of which surfaces are coated with simple gold or platinum substance, or a complex of gold and platinum and which have an average particle diameter of 1-100 nm and a binder matrix as main constituents. The transparent conductive base material has an excellent reflection prevention effect and transmitted light ray profile as compared with a conventional transparent conductive base material and also has good weather resistance

and conductivity. In addition, a display device to which the transparent conductive base material is applied can restrain the surface reflection of the display screen and has a high electric-field shielding effect.

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 CLAIMS

[Claim(s)]

[Claim 1] The transparent conductive base material characterized by the above-mentioned transparence conductive layer using as a principal component the noble-metals coat silver particle of 1-100nm of mean diameters by which coating of gold, a platinum simple substance, or the complex of gold and platinum was carried out to the front face of a silver particle, and the binder matrix in a transparence substrate and the transparent conductive base material equipped with the transparence two-layer film which consisted of a transparence conductive layer by which sequential formation was carried out, and a transparence coat layer on this transparence substrate.

[Claim 2] The transparent conductive base material according to claim 1 with which the amount of coatings of the gold in the above-mentioned noble-metals coat silver particle, a platinum simple substance, or the complex of gold and platinum is characterized by being set as the range of the 5 - 100 weight section to the silver 100 weight section.

[Claim 3] The transparent conductive base material according to claim 1 or 2 characterized by containing the conductive oxide particle in the above-mentioned transparence conductive layer.

[Claim 4] The transparent conductive base material according to claim 3 characterized by the above-mentioned conductive oxide particles being one or more sorts of particles chosen from tin oxide, the tin antimonite acid ghost, or the indium stannic acid ghost.

[Claim 5] The transparent conductive base material according to claim 1 to 4 with which the above-mentioned binder matrix and transparence coat layer of a transparence conductive layer are characterized by using silicon oxide as a principal component.

[Claim 6] The transparent conductive base material according to claim 1 to 5 characterized by for the surface electrical resistance of the above-mentioned transparence conductive layer being 10-3000ohm/**, and the standard deviation of the permeability of only the transparence two-layer film which does not contain the above-mentioned transparence substrate in each wavelength in every 5nm of a visible-ray wavelength region (380-780nm) being 0 - 5%.

[Claim 7] The manufacture approach of the transparent conductive base material characterized by heat-treating after applying the coating liquid for transparence conductive layer formation which uses as a principal component a noble-metals coat silver particle with a mean particle diameter of 1-100nm distributed by a solvent and this solvent in the manufacture approach of a transparent conductive base material according to claim 1 on the above-mentioned transparence substrate and applying the coating liquid for transparence coat stratification subsequently.

[Claim 8] The manufacture approach of a transparent conductive base material according to claim 7 that the amount of coatings of the gold in the above-mentioned noble-metals coat silver particle, a platinum simple substance, or the complex of gold and platinum is characterized by being set as the range of the 5 - 100 weight section to the silver 100 weight section.

[Claim 9] The manufacture approach of the transparent conductive base material according to claim 7 or 8 characterized by containing the conductive oxide particle in the above-mentioned coating liquid for transparence conductive layer formation.

[Claim 10] The manufacture approach of the transparent conductive base material according to claim 9 characterized by the above-mentioned conductive oxide particles being one or more sorts of particles chosen from tin oxide, the tin antimonite acid ghost, or the indium stannic acid ghost.

[Claim 11] The manufacture approach of the transparent conductive base material according to claim 7 to 10 characterized by containing the inorganic binder which constitutes the binder matrix of a transparent conductive layer in the above-mentioned coating liquid for transparent conductive layer formation.

[Claim 12] The manufacture approach of a transparent conductive base material according to claim 7 to 11 that the above-mentioned coating liquid for transparent coat stratification is characterized by using the silica sol as a principal component.

[Claim 13] The display characterized by for a transparent conductive base material according to claim 1 to 6 carrying out that transparent two-layer film side outside, and incorporating it as the above-mentioned front plate in a display equipped with the body of equipment, and the front plate arranged at this front-face side.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention is equipped with the transparence two-layer film which consists of the transparence conductive layer by which sequential formation was carried out, and a transparence coat layer a transparence substrate and on this. For example, the Braun tube (CRT), a plasma display panel (PDP), The transparent conductive base material used for the front plate of displays, such as a fluorescent display (VFD) and a liquid crystal display (LCD), etc. is started. It is related with the display with which amelioration and its manufacture approach of the transparent conductive base material which is excellent in weatherability, conductivity, etc. and can moreover aim at reduction of a manufacturing cost especially, and this transparent conductive base material were applied.

[0002]

[Description of the Prior Art] The environment where many OA equipment must be introduced into office by office automation(OA)-ization in recent years, the display of OA equipment must be faced, and it must work all day is not new recently.

[0003] By the way, when working in contact with the cathode-ray tube (: called the above-mentioned Braun tube CRT) of a computer etc. as an example of OA equipment, the display screen is legible and it is required that there are no adhesion of dust and electric shock shock by electrification of a CRT front face out of not impressing visual fatigue etc. Furthermore, in addition to this etc., we are anxious about the adverse effect to the body of a low frequency electromagnetic wave generated from CRT, and, recently, such an electromagnetic wave is wanted not to be revealed outside to CRT.

[0004] And it generates from a deflecting coil or a flyback transformer, and the above-mentioned electromagnetic wave has the electromagnetic wave of a large quantity in the inclination revealed to a perimeter increasingly with enlargement of television.

[0005] By the way, leakage of a field can prevent most with the device of changing the configuration of a deflecting coil. It is possible to also prevent leakage of electric field on the other hand by forming a transparence conductive layer in the glass front front face of CRT.

[0006] The prevention approach for leakage of such electric field is the same in recent years on the cure and principle target which have been taken for electrification prevention. however, the above-mentioned transparence conductive layer -- antistatic -- conductivity far higher than the conductive layer currently formed in business is searched for. namely, antistatic -- business -- surface electrical resistance -- 108 omega / ** extent -- enough -- ** -- although carried out, in order to prevent leakage electric field (electric-field shielding) -- at least 106 It is necessary to form the transparence conductive layer of the low resistance which is below 103ohms / ** preferably below omega/**.

[0007] Then, although some proposals are made from before in order to cope with the above-mentioned demand, the method of calcinating the coating liquid for transparence conductive layer formation which distributed the conductive particle in the solvent with inorganic binders, such as alkyl silicate, at the temperature of 200 degrees C or less after spreading / desiccation to the glass front of CRT is learned as an approach that it is low cost also in it, and low surface electrical resistance can be realized.

[0008] And the approach using this coating liquid for transparence conductive layer formation is far simple compared with the formation approach of other transparence conductive layers, such as vacuum deposition and a spatter, is low, and is a very advantageous approach as electric-field shielding which can be processed to CRT. [of a manufacturing cost]

[0009] As the above-mentioned coating liquid for transparence conductive layer formation used for this approach, what applied the indium stannic acid ghost (ITO) to the conductive particle is known. However, the surface electrical resistance of the film obtained is 104-106. Since it was high and the amendment circuit for electric-field cancellation was [being omega/being **, and] needed for fully covering leakage electric field, there was a problem from which the part and a manufacturing cost become comparatively high-priced. On the other hand, although membranous permeability becomes low a little compared with the coating liquid which used ITO in the coating liquid for transparence conductive layer formation which used the metal powder for the above-mentioned conductive particle, it is 102-103. The low resistance film omega/** is obtained. Therefore, it is thought that it becomes advantageous in cost since the amendment circuit mentioned above becomes unnecessary, and it will become the mainstream from now on.

[0010] And it is restricted to noble metals, such as the silver and gold which cannot oxidize easily in air as a metal particle applied to the above-mentioned coating liquid for transparence conductive layer formation as shown in JP,8-77832,A, JP,9-55175,A, etc., platinum, a rhodium, and palladium. This is because an oxide film will surely be formed in the front face of metal particles, such as this, under an atmospheric-air ambient atmosphere and conductivity good as a transparence conductive layer is no longer acquired, when metal particles other than noble metals, for example, iron, nickel, cobalt, etc. are applied.

[0011] Moreover, on the other hand, in order to make the display screen legible, giving anti-glare treatment to a face panel front face, and suppressing an echo of a screen is also performed. Although made also by the approach to which prepare detailed irregularity and surface diffuse reflection is made to increase, this anti-glare treatment cannot be said as a not much desirable approach, in order that resolution may fall and image quality may fall off, when this approach is used. Therefore, it is desirable to perform anti-glare treatment with the interference method which controls the refractive index and thickness of a transparence coat so that the reflected light may produce destructive interference to incident light rather. In order to acquire a low reflection effect with such an interference method, the two-layer structure film which generally set the optical thickness of the high refractive-index film and the low refractive-index film as $1/4\lambda$, $1/4\lambda$ or $1/2\lambda$, and $1/4\lambda$, respectively is adopted, and the film which consists of the above-mentioned indium stannic acid ghost (ITO) particle is also used as this kind of high refractive-index film.

[0012] In addition, in a metal, among optical constants (n - ik , n :refractive index, $i^2 = -1$, k : extinction coefficient), although the value of n is small, even when the transparence conductive layer which the value of k becomes from a metal particle since it is extremely large compared with ITO etc. is used, the acid-resisting effectiveness by interference of light is acquired by the two-layer structure film like ITO (high refractive-index film).

[0013]

[Problem(s) to be Solved by the Invention] By the way, although it is limited to noble metals, such as silver, gold, platinum, a rhodium, and palladium, as a metal particle applied to the conventional coating liquid for transparence conductive layer formation as mentioned above When electric resistance, such as this, is compared, the specific resistance of platinum, a rhodium, and palladium It was more advantageous to apply a silver particle metallurgy particle by 10.6 and 5.1 or 10.8micro ohm-cm for forming the low transparence conductive layer of surface electrical resistance, since it is high compared with 1.62 or 2.2micro ohm-cm of silver and gold, respectively.

[0014] However, when a silver particle is applied, sulfuration and degradation by brine are intense, the problem was in weatherability, and when another side and a golden particle were applied, although the problem of the above-mentioned weatherability was lost, it had the problem on cost like the case where a platinum particle, a rhodium particle, a palladium particle, etc. are applied. Furthermore, when a

golden particle is applied, in order for the transparense conductive layer itself formed of the optical property peculiar to gold to absorb a part of visible ray, in the screen of displays, such as CRT as which a flat transmitted-light profile is required throughout a visible ray, it had the inapplicable trouble.

[0015] The place which this invention was made paying attention to such a trouble, and is made into that technical problem is to excel in weatherability, conductivity, etc., offer the transparent conductive base material which can moreover aim at reduction of a manufacturing cost, and its manufacture approach, and offer the display with which the transparent conductive base material of a doubling lever was applied.

[0016]

[Means for Solving the Problem] Namely, invention concerning claim 1 is premised on a transparense substrate and the transparent conductive base material equipped with the transparense two-layer film which consisted of a transparense conductive layer by which sequential formation was carried out, and a transparense coat layer on this transparense substrate. It is characterized by the above-mentioned transparense conductive layer using as a principal component the noble-metals coat silver particle of 1-100nm of mean diameters by which coating of gold, a platinum simple substance, or the complex of gold and platinum was carried out to the front face of a silver particle, and the binder matrix. Moreover, invention concerning claim 2 is premised on the transparent conductive base material concerning invention according to claim 1. The amount of coatings of the gold in the above-mentioned noble-metals coat silver particle, a platinum simple substance, or the complex of gold and platinum is characterized by being set as the range of the 5 - 100 weight section to the silver 100 weight section.

[0017] Next, invention which invention concerning claim 3 is characterized by containing the conductive oxide particle in the above-mentioned transparense conductive layer on the assumption that the transparent conductive base material concerning invention according to claim 1 or 2, and relates to claim 4 is characterized by the above-mentioned conductive oxide particles being one or more sorts of particles chosen from tin oxide, the tin antimonite acid ghost, or the indium stannic acid ghost a premise [a transparent conductive base material according to claim 3].

[0018] Moreover, invention concerning claim 5 is premised on a transparent conductive base material according to claim 1 to 4. Invention which the above-mentioned binder matrix and transparense coat layer of a transparense conductive layer are characterized by using silicon oxide as a principal component, and requires them for claim 6 The surface electrical resistance of the above-mentioned transparense conductive layer is 10-3000ohm/** on the assumption that a transparent conductive base material according to claim 1 to 5. And it is characterized by the standard deviation of the permeability of only the transparense two-layer film which does not contain the above-mentioned transparense substrate in each wavelength in every 5nm of a visible-ray wavelength region (380-780nm) being 0 - 5%.

[0019] Next, invention concerning claims 7-12 relates to invention which specified the manufacture approach of the above-mentioned transparent conductive base material.

[0020] Namely, invention concerning claim 7 is premised on the manufacture approach of a transparent conductive base material according to claim 1. The coating liquid for transparense conductive layer formation which uses as a principal component a noble-metals coat silver particle with a mean particle diameter of 1-100nm distributed by a solvent and this solvent is applied on the above-mentioned transparense substrate. Subsequently, invention which is characterized by heat-treating and relates to claim 8 after applying the coating liquid for transparense coat stratification The amount of coatings of the gold in the above-mentioned noble-metals coat silver particle, a platinum simple substance, or the complex of gold and platinum is characterized by being set as the range of the 5 - 100 weight section to the silver 100 weight section a premise [the manufacture approach of a transparent conductive base material according to claim 7].

[0021] Moreover, invention concerning claim 9 is premised on the manufacture approach of a transparent conductive base material according to claim 7 or 8. Invention which is characterized by containing the conductive oxide particle and starts in the above-mentioned coating liquid for transparense conductive layer formation at claim 10 The above-mentioned conductive oxide particle is

characterized by being one or more sorts of particles chosen from tin oxide, the tin antimonate acid ghost, or the indium stannate acid ghost a premise [the manufacture approach of a transparent conductive base material according to claim 9].

[0022] Moreover, invention concerning claim 11 is premised on the manufacture approach of a transparent conductive base material according to claim 7 to 10. Invention which is characterized by containing the inorganic binder which constitutes the binder matrix of a transparent conductive layer, and starts in the above-mentioned coating liquid for transparent conductive layer formation at claim 12. The above-mentioned coating liquid for transparent coat stratification is characterized by using the silica sol as a principal component a premise [the manufacture approach of a transparent conductive base material according to claim 7 to 11].

[0023] Next, invention concerning claim 13 is characterized by for a transparent conductive base material according to claim 1 to 6 carrying out that transparent two-layer film side outside, and incorporating it as the above-mentioned front plate, on the assumption that a display equipped with the body of equipment, and the front plate arranged at this front-face side.

[0024]

[Embodiment of the Invention] Hereafter, the gestalt of operation of this invention is explained to a detail.

[0025] First, gold or platinum of this invention is chemically stable, and since it excels in weatherability, chemical resistance, oxidation resistance, etc., if the front face of a silver particle is coated with gold, a platinum simple substance, or the complex of gold and platinum, it is based on the view that the chemical stability can be raised. Moreover, the electric resistance of platinum is high a little compared with silver and gold, as mentioned above, but since the complex ingredient of gold, a platinum simple substance or gold, and platinum is applied as a coating layer of the above-mentioned silver particle front face, it does not spoil good silver conductivity. In addition, although the method of making gold, platinum, or a golden list alloy silver with platinum, considering as an alloy particle, and making properties, such as weatherability mentioned above, improve is also considered instead of coating a silver particle with the above-mentioned gold, a platinum simple substance, or the complex of gold and platinum. By this approach, a lot of gold, platinum or gold, and platinum are needed from it being necessary to make high concentration of the gold in the whole particle, a platinum simple substance or gold, and platinum, and there is difficulty in cost. From the above idea, the solution of the trouble mentioned above by applying the noble-metals coat silver particle to which coating of gold, a platinum simple substance, or the complex of gold and platinum was carried out of drawing is in the front face of a silver particle in this invention as a metal particle in the coating liquid for transparent conductive layer formation.

[0026] That is, if the front face of a silver particle is coated with gold, a platinum simple substance, or the complex of gold and platinum, since the silver inside a noble-metals coat silver particle will be protected by gold, a platinum simple substance, or the complex of gold and platinum, weatherability, chemical resistance, etc. are improved remarkably. For example, although the silver particle of the chloride ion in brine and a transparent conductive layer will react, it will deteriorate remarkably in a short time of less than 1 hour and even exfoliation of the film in a transparent conductive layer will be produced if immersed in brine 5%, the transparent conductive layer which consists of a silver particle and the binder matrix which uses silicon oxide as a principal component. In the case of the transparent conductive layer which applied the noble-metals coat silver particle to which coating of gold, a platinum simple substance, or the complex of gold and platinum was carried out. Although based also on the amount of coatings of gold, a platinum simple substance or gold, and platinum complex, even immersion of 24 hours or more does not change at all, but, as for a transparent conductive layer, shows the outstanding weatherability. Moreover, in order that platinum may not oxidize in atmospheric air in a golden list, there is also no degradation of the electric resistance by oxidation, and the transparent conductive layer to which the noble-metals coat silver particle was applied is superior to the surface electrical resistance of the transparent conductive layer to which the silver particle was applied.

[0027] Here, the above-mentioned noble-metals coat silver particle in this invention requires that the

mean particle diameter is 1-100nm (claim 1). In the case of less than 1nm, manufacture of this particle is difficult, and is easy to condense and is not still more practical in coating liquid. Moreover, it is because surface electrical resistance becomes high too much and is not practical even when the visible-ray permeability of the formed transperence conductive layer becomes low too much, thickness is set up thinly temporarily and visible-ray permeability is made high if 100nm is exceeded. In addition, mean particle diameter here shows the mean particle diameter of the particle observed with a transmission electron microscope (TEM).

[0028] Next, as for the amount of coatings of gold, a platinum simple substance or gold, and platinum complex, in the above-mentioned noble-metals coat silver particle, it is [to set it as the range of 10 - 50 weight section preferably desirably (claim 2)] good to set it as the range of the 5 - 100 weight section to the silver 100 weight section. It is because there is difficulty in cost when the protective effect of coating may become weaker, weatherability may worsen a little, if the amount of coatings of gold, a platinum simple substance or gold, and platinum complex is under 5 weight sections, and the 100 weight sections are exceeded conversely.

[0029] In addition, one or more sorts of conductive oxide particles chosen from tin oxide, the tin antimonie acid ghost, or the indium stannic acid ghost into the transperence conductive layer may be added in order to aim at improvement in the film transmission in a transperence conductive layer (claim 3, claim 4). in this case, the compounding ratio of the noble-metals coat silver particle in a transperence conductive layer, and a conductive oxide particle -- the noble-metals coat silver particle 100 weight section -- receiving -- the conductive oxide particle 1 - the 200 weight sections -- it is good to set it as the range of the 10 - 100 weight section preferably. It is because resistance of a transperence conductive layer becomes high too much and is not practical if the effectiveness of conductive oxide particle addition will not be seen if the loadings of a conductive oxide particle are under 1 weight section, but the 200 weight sections are exceeded conversely. Moreover, the mean particle diameter of a conductive oxide particle has desirable about 1-100nm like the above-mentioned noble-metals coat silver particle.

[0030] Next, the coating liquid for transperence conductive layer formation containing the above-mentioned noble-metals coat silver particle can manufacture this by the following approaches. namely, known approach [, for example, Carey-Lea, -- by law, Am.J.Sci., 37 and 47 (1889), Am.J.Sci., and 38 (1889)] After preparing the colloidal dispersion liquid of a silver particle, reducing agents, such as a hydrazine, are added to these dispersion liquid. Furthermore, by adding the solution of an aurate or platinate, or the mixed solution of an aurate and platinate there, coating of gold, a platinum simple substance or gold, and platinum complex is performed to a silver particle, and noble-metals coat silver particle dispersion liquid are obtained. In addition, it is also possible to prepare the noble-metals coat silver particle dispersion liquid to which it replaced with the approach using the above-mentioned mixed solution of an aurate and platinate, the solution of an aurate and the solution of platinate were independently added, and coating of gold and the platinum complex was carried out. Moreover, the little dispersant of the colloidal dispersion liquid of a silver particle, the solution of an aurate, the solution of platinate, and the mixed solution of an aurate and platinate may be added to any one or each at least as occasion demands at the coating process of gold, a platinum simple substance or gold, and platinum complex. Then, it is desirable to lower the electrolytic concentration in dispersion liquid by approaches, such as dialysis, electrodialysis, the ion exchange, and an ultrafiltration. This is because colloid will generally be condensed with an electrolyte if electrolytic concentration is not lowered, and this phenomenon is known also as a Schulze-Hardy rule. In addition, since it is the same, also when blending the conductive oxide particle chosen from tin oxide, the tin antimonie acid ghost, or the indium stannic acid ghost into the above-mentioned noble-metals coat silver particle dispersion liquid or the coating liquid for transperence conductive layer formation, it is desirable to fully perform demineralization of conductive oxide particles, such as this, or the dispersion liquid of those. And the quality governings (particle concentration, moisture concentration, etc.) by addition of concentration dehydration from the obtained noble-metals coat silver particle dispersion liquid, an organic solvent, etc. are made eventually, and the above-mentioned coating liquid for transperence conductive layer formation is prepared. In this coating liquid for transperence conductive layer formation, the antecedent basis of coating of gold, a

platinum simple substance, or the complex of gold and platinum being carried out to the silver particle front face. In the particle observation and component analysis (EDX: energy dispersion mold X-ray-analysis equipment) by the transmission electron microscope (TEM), it is before and after coating of gold, a platinum simple substance or gold, and platinum complex, and particle diameter is hardly changing. And distribution of gold, a platinum simple substance or gold, and platinum complex is uniform to each particle. Furthermore, it is technically checked from the coordination number of the gold in EXAFS (Extended X-ray Absorption Fine Structure: broader-based X-ray absorption fine structure) analysis, a platinum simple substance or gold, and platinum complex.

[0031] In addition, about the coat gestalt of gold and platinum complex over a silver particle, the solution of an aurate and the solution of platinate are applied at the coating process of gold and platinum complex, or the mixed solution of an aurate and platinate is applied -- that difference -- moreover, various kinds of gestalten can be considered by the combination timing of solutions, such as this, the difference in the concentration of the aurate and platinate to apply, etc. That is, gold covers all front faces or a part of silver particle with the difference among conditions, such as this, and platinum has covered that whole or the gestalt which it was reverse, and platinum covered all front faces or a part of silver particle, and has been covered with this condition of platinum and gold being simple substances, respectively, or having been alloyed, without gold's having covered that whole or lapping all the front faces of a silver particle mutually can be considered.

[0032] Moreover, in the above-mentioned approach, the coating reaction of the gold to a silver particle front face, a platinum simple substance or gold, and platinum complex occur, because a detailed silver particle already exist so much in liquid, and in case gold and platinum arise by reduction of an aurate and platinate, it be because it go on on the conditions in energy with more advantageous grow up to be the front face by use a silver particle as a nucleus rather than gold and platinum carry out karyogenesis (homogeneity karyogenesis) independently.

[0033] Thus, that body consists of transparence two-layer film by which the transparent conductive base material concerning this invention consists of transparence substrates, such as a glass substrate and a plastic plate, and the lower layer of the transparence conductive layer to which the noble-metals coat silver particle of 1-100nm of mean diameters by which it was formed on this transparence substrate, and a binder matrix are used as a principal component, and the upper layer of a transparence coat layer formed on this transparence conductive layer.

[0034] And for forming the above-mentioned transparence two-layer film on a transparence substrate, this can be performed by the following approaches. For example, after applying the coating liquid for transparence conductive layer formation which uses as a principal component a noble-metals coat silver particle with a mean particle diameter of 1-100nm distributed by a solvent and this solvent on transparence substrates, such as a glass substrate and a plastic plate, by the technique of a spray coat, a spin coat, a wire bar coat, a doctor blade coat, etc. and drying if needed, an overcoat is carried out by the technique of having mentioned above the coating liquid for transparence coat stratification which uses a silica sol etc. as a principal component. Next, after carrying out an overcoat, the coating liquid for transparence coat stratification which heat-treated and carried out the overcoat at the temperature of about 50-250 degrees C is hardened, and the above-mentioned transparence two-layer film is formed (claim 7). In addition, in heat-treatment of about 50-250 degrees C, since the noble-metals coat silver particle is protected with gold, a platinum simple substance, or the complex of gold and platinum, a problem is not produced, but when it exceeds 200 degrees C as it is a silver particle, a surface-electrical-resistance value rises by oxidation diffusion, and degradation of the film arises.

[0035] When an overcoat is carried out by the technique of having mentioned above the coating liquid for transparence coat stratification which uses a silica sol etc. as a principal component here, In the gap of the noble-metals coat silver particle layer formed with the coating liquid for transparence coat stratification used as a principal component, the noble-metals coat silver particle applied beforehand It is that the silica sol liquid (this silica sol liquid serves as a binder matrix which uses silicon oxide as a principal component by the above-mentioned heat-treatment) which carried out the overcoat sinks in, and conductive improvement, improvement in reinforcement, and much more improvement in

weatherability are attained simultaneously. Furthermore, in the optical constant ($n-ik$) of the transparence conductive layer distributed in the above-mentioned binder matrix to which a noble-metals coat silver particle uses silicon oxide as a principal component, although a refractive index n is not so large, since it is large, an extinction coefficient k can fall the reflection factor of the transparence two-layer film substantially according to the transparence two-layer membrane structure of the above-mentioned transparence conductive layer and a transparence coat layer. And as shown in drawing 1, even if it compares with the case where an ITO particle (example 2 of a comparison) and a silver particle (example 1 of a comparison) are applied, when the noble-metals coat silver particle (example 1) to which coating of the golden simple substance was carried out is used, a reflection factor is improved in the short wavelength region (380-500nm) of a visible ray. Moreover, the transmitted-light profile of the transparence two-layer film is also improved by coating a silver particle with a golden simple substance in the short wavelength region of a visible ray, as shown in drawing 2. For example, although there is about 7% about the permeability of only the transparence two-layer film which does not contain the transparence substrate in each wavelength in every 5nm of a visible-ray wavelength region (380-780nm) when the standard deviation is compared, and a silver particle (example 1 of a comparison) is used a silver particle -- a noble-metals coat -- carrying out (examples 1-11) -- it becomes about 2 - 3% of small value, and the very flat transparency profile is obtained (claim 6). Although it is not yet clear about the reason an echo of the these transparence two-layer film and a transparency property are improved, change of the surface plasmon of the metal particle by having coated the silver particle with gold, a platinum simple substance, or the complex of gold and platinum can be considered.

[0036] Here, as a silica sol applied to the above-mentioned coating liquid for transparence coat stratification, water and an acid catalyst can be added to alt.alkyl silicate, it can hydrolyze, and the polymerization object as for which the polymerization object to which dehydration condensation polymerization was advanced, or the alkyl silicate solution of marketing to which hydrolysis condensation polymerization was already advanced to 4 - a pentamer advanced hydrolysis and dehydration condensation polymerization further can be used. In addition, if dehydration condensation polymerization advances, since solution viscosity will rise and it will solidify eventually, about the degree of dehydration condensation polymerization, it adjusts to the place below the upper limit viscosity which can be applied on transparence substrates, such as a glass substrate and a plastic plate. However, especially if the degree of dehydration condensation polymerization is the level below the above-mentioned upper limit viscosity, it will not be specified, but when film reinforcement, weatherability, etc. are taken into consideration, 500 to about 3000 are desirable at weight average molecular weight. . And at the time of heating baking of the transparence two-layer film, a dehydration condensation polymerization reaction completes an alkyl silicate partial hydrolysis polymerization object mostly, and it becomes the hard silicate film (film which uses silicon oxide as a principal component). In addition, it is also possible to add a magnesium flux particle, alumina sol, a titania sol, a zirconia sol, etc. to the above-mentioned silica sol, to adjust the refractive index of a transparence coat layer, and to change the reflection factor of the transparence two-layer film.

[0037] Moreover, in addition to the noble-metals coat silver particle of 1-100nm of mean diameters distributed by a solvent and this solvent, in the formation process of the above-mentioned transparence conductive layer, the coating liquid for transparence conductive layer formation with which the silica sol liquid as an inorganic binder component which constitutes a binder matrix was blended may be used (claim 11). Also in this case, the coating liquid for transparence conductive layer formation with which silica sol liquid is contained is applied, and the same transparence two-layer film is obtained by carrying out an overcoat by the technique of having mentioned above the coating liquid for transparence coat stratification, after making it dry if needed. In addition, since it is the same as that of the case where a conductive oxide particle is blended in the coating liquid for transparence conductive layer formation, it is desirable to fully perform the demineralization also about the above-mentioned silica sol liquid blended in the coating liquid for transparence conductive layer formation.

[0038] Since the transparent conductive base material applied to this invention as explained above has the acid-resisting effectiveness and the transmitted-light profile superior to conventionally and has good

weatherability and a high electric-field shielding effect, it is applicable to the front plate which constitutes the part in displays, such as the Braun tube (CRT) mentioned above, a plasma display panel (PDP), a fluorescent display (VFD), a field emission display (FED), an electroluminescence display (ELD), and a liquid crystal display (LCD).

[0039]

[Example] Hereafter, although the example of this invention is explained concretely, this invention is not limited to these examples. Moreover, "%" in the text shows "% of the weight" except for permeability, a reflection factor, and haze (% of a value), and the "section" shows the "weight section."

[0040] Carey-Lea of the [example 1] above-mentioned -- the colloidal dispersion liquid of a silver particle was prepared by law. After adding 39g of iron(II) sulfate water solutions, and the mixed liquor of 48g of 37.5% sodium-citrate water solutions to 33g of silver-nitrate water solutions 23% 9% and specifically filtering and washing sediment, pure water was added and the colloidal dispersion liquid (Ag:0.45%) of a silver particle was prepared. Having added 0.5g of hydrazine water solutions to 15g of colloidal dispersion liquid of this silver particle 1%, and stirring, 15g (Au:0.1%) of auric acid potassium [KAu (OH)₄] water solutions and the mixed liquor of 0.3g of 2% giant-molecule dispersant water solutions were added, and the colloidal dispersion liquid of a noble-metals coat silver particle with which coating of the golden simple substance was carried out was obtained. After desalting the colloidal dispersion liquid of this noble-metals coat silver particle with ion exchange resin (Mitsubishi Chemical trade name diamond ion SK1B, SA20AP), ethanol (EA) and diacetone alcohol (DAA) were added to the liquid condensed by ultrafiltration, and the coating liquid for transparence conductive layer formation (Ag:0.217%, Au:0.057%, water: 11.8%, EA:82.9%, DAA:5.0%) with which a noble-metals coat silver particle is contained was obtained. As a result of observing the obtained coating liquid for transparence conductive layer formation with a transmission electron microscope, the mean particle diameter of a noble-metals coat silver particle was 7.2nm.

[0041] Next, the coating liquid for transparence conductive layer formation with which a noble-metals coat silver particle is contained On the glass substrate (soda lime glass with a thickness of 3mm) heated by 40 degrees C The transparence conductive layer which carries out the spin coat (for 130rpm and 60 seconds) of the silica sol liquid, is made to harden 180 degrees C for 20 minutes further continuously, and contains a noble-metals coat silver particle after carrying out a spin coat (for 130rpm and 60 seconds), The glass substrate with the transparence two-layer film which consisted of transparence coat layers which consist of the silicate film which uses silicon oxide as a principal component, i.e., the transparent conductive base material concerning an example 1, was obtained.

[0042] The above-mentioned silica sol liquid methyl silicate 51 (trade name by the COL coat company) here The 19.6 sections, The ethanol 57.8 section, the 1% nitric-acid water-solution 7.9 section, and the pure-water 14.7 section are used. SiO₂ That whose solid content (silicon oxide) concentration is 10% is prepared, and it is SiO₂ eventually. It diluted with the mixture (IPA/NBA=3/1) of isopropyl alcohol (IPA) and n-butanol (NBA), and has obtained so that solid content concentration may become 0.7%.

[0043] And the film property (the standard deviation of surface electrical resistance, visible-ray transmission, and transmission, a haze value, a bottom product reflection factor / bottom product wavelength) of the transparence two-layer film formed on the glass substrate is shown in the following table 1. In addition, the above-mentioned bottom product reflection factor means the minimum reflection factor in the reflective profile of a transparent conductive base material, and bottom product wavelength means wavelength [in / in a reflection factor / the minimum]. Moreover, the reflective profile of the transparent conductive base material concerning the manufactured example 1 is doubled with drawing 1 and drawing 3 , and a transparency profile is doubled with drawing 2 and drawing 4 , and it is shown.

[0044] In addition, the permeability of only the transparence two-layer film which does not contain the transparence substrate (glass substrate) in each wavelength in every 5nm of a visible-ray wavelength region (380-780nm) in a table 1 is called for as follows. permeability (%) =[(permeability measured whole transparence substrate)/(permeability of transparence substrate)] x100 [namely,] of only the transparence two-layer film which does not contain a transparence substrate -- here, especially in this

description, unless reference is made, as permeability, the value measured the whole transparence substrate (that is, the thing of the transparence two-layer film containing a transparence substrate means the above-mentioned transparent conductive base material) is used.

[0045] Moreover, the surface electrical resistance of the transparence two-layer film was measured using Mitsubishi Chemical surface-electrical-resistance meter RORESUTA AP (MCP-T400). A haze value and visible-ray permeability were measured using every transparence substrate and the Murakami Color Research Laboratory hazemeter (HR-200). The reflection factor and echo / transparency profile were measured using the spectrophotometer (U-4000) by Hitachi, Ltd. Moreover, the JEOL transmission electron microscope is estimating the particle size of a noble-metals coat silver particle.

[0046] The colloidal dispersion liquid of a silver particle prepared by the same approach as the [example 2] example 1 is used. A hydrazine water solution and an auric acid potassium water solution (Au:0.15%) are used 1.5%. the coating liquid for transparence conductive layer formation (Ag: -- 0.221%) which the noble-metals coat silver particle with a mean particle diameter of 6.3nm distributed Au: 0.079%, water : 5.0%, EA:89.7%, and DAA:5.0% are obtained. And SiO₂ of silica sol liquid except having diluted so that solid content (silicon oxide) concentration might become 0.65% It carried out like the example 1 and the glass substrate with the transparence two-layer film which consisted of a transparence conductive layer containing a noble-metals coat silver particle and a transparence coat layer which consists of the silicate film which uses silicon oxide as a principal component, i.e., the transparent conductive base material concerning an example 2, was obtained.

[0047] And the film property of the transparence two-layer film formed on the glass substrate is shown in the following table 1. Moreover, the reflective profile of the transparent conductive base material concerning the manufactured example 2 is shown in drawing 5 , and a transparency profile is shown in drawing 6 .

[0048] The colloidal dispersion liquid of a silver particle prepared by the same approach as the [example 3] example 1 is used. A hydrazine water solution and an auric acid potassium water solution (Au:0.05%) are used 0.5%. the coating liquid for transparence conductive layer formation (Ag: -- 0.24%) which the noble-metals coat silver particle with a mean particle diameter of 6.8nm distributed Au: 0.028%, water : 3.7%, EA:91.0%, and DAA:5.0% are obtained. And SiO₂ of silica sol liquid except having diluted so that solid content (silicon oxide) concentration might become 0.65% It carried out like the example 1 and the glass substrate with the transparence two-layer film which consisted of a transparence conductive layer containing a noble-metals coat silver particle and a transparence coat layer which consists of the silicate film which uses silicon oxide as a principal component, i.e., the transparent conductive base material concerning an example 3, was obtained.

[0049] The film property of the transparence two-layer film formed on the glass substrate is shown in the following table 1.

[0050] Agitating using the colloidal dispersion liquid of a silver particle prepared by the same approach as the [example 4] example 1 without adding the hydrazine water solution as a reducing agent 15g (Au:0.05%) of auric acid potassium water solutions is added. By the substitution reaction of gold and silver the coating liquid for transparence conductive layer formation (Ag: -- 0.245%) which obtained the colloidal dispersion liquid of a noble-metals coat silver particle, and the noble-metals coat silver particle with a mean particle diameter of 6.5nm distributed Au: 0.025%, water : except having obtained 7.6%, EA:87.1%, and DAA:5.0% It carried out like the example 1 and the glass substrate with the transparence two-layer film which consisted of a transparence conductive layer containing a noble-metals coat silver particle and a transparence coat layer which consists of the silicate film which uses silicon oxide as a principal component, i.e., the transparent conductive base material concerning an example 4, was obtained.

[0051] The film property of the transparence two-layer film formed on the glass substrate is shown in the following table 1.

[0052] The solution which the noble-metals coat silver particle with a mean particle diameter of 7.1nm distributed using 0.4g of hydrazine water solutions and an auric acid potassium water solution (Au:0.075%) 1% was obtained using the colloidal dispersion liquid of a silver particle prepared by the

same approach as the [example 5] example 1. next, the inside of this solution -- the indium stannic acid ghost (ITO) particle (the Sumitomo Metal Mining Co., Ltd. make --) of 0.03 micrometers of mean diameters The ITO dispersion liquid which fully desalted according to the ion exchange and were obtained, using trade name SUFP-HX are added. the coating liquid for transperence conductive layer formation (Ag: -- 0.294%) which the noble-metals coat silver particle and the ITO particle distributed eventually Au: 0.049%, ITO:0.1%, water : 9.7%, EA:84.95%, DAA: Obtain 4.9%, and weight average molecular weight uses the silica sol liquid of 1920, and it is SiO₂. While using the glass substrate which diluted so that solid content (silicon oxide) concentration might become 0.8%, and was heated by 35 more degrees C Except having carried out the spin coat of the coating liquid for transperence conductive layer formation, and the silica sol liquid the condition for 60 seconds by 150rpm, and having stiffened 210 degrees C for 20 minutes It carried out like the example 1 and the glass substrate with the transperence two-layer film which consisted of a transperence conductive layer containing a noble-metals coat silver particle and an ITO particle and a transperence coat layer which consists of the silicate film which uses silicon oxide as a principal component, i.e., the transparent conductive base material concerning an example 5, was obtained.

[0053] And the film property of the transperence two-layer film formed on the glass substrate is shown in the following table 1. Moreover, the reflective profile of the transparent conductive base material concerning the manufactured example 5 is shown in drawing 7 , and a transparency profile is shown in drawing 8 .

[0054] The solution which the noble-metals coat silver particle with a mean particle diameter of 7.1nm distributed using 0.4g of hydrazine water solutions and an auric acid potassium water solution (Au:0.075%) 1% was obtained using the colloidal dispersion liquid of a silver particle prepared by the same approach as the [example 6] example 1. next, the inside of this solution -- the antimony stannic acid ghost (ATO) particle (the Ishihara Sangyo Kaisha, Ltd. make --) of 0.01 micrometers of mean diameters The ATO dispersion liquid which fully desalted according to the ion exchange and were obtained, using trade name SN-100P are added. the coating liquid for transperence conductive layer formation (Ag: -- 0.29%) which the noble-metals coat silver particle and the ATO particle distributed eventually Au: 0.048%, ATO:0.174%, water : 11.0% and EA:83.58 and DAA:4.9% are obtained. And weight average molecular weight uses the silica sol liquid of 1920, and it is SiO₂. While using the glass substrate which diluted so that solid content (silicon oxide) concentration might become 0.8%, and was heated by 35 more degrees C Except having carried out the spin coat of the coating liquid for transperence conductive layer formation, and the silica sol liquid the condition for 60 seconds by 150rpm, and having stiffened 210 degrees C for 20 minutes It carried out like the example 1 and the glass substrate with the transperence two-layer film which consisted of a transperence conductive layer containing a noble-metals coat silver particle and an ATO particle and a transperence coat layer which consists of the silicate film which uses silicon oxide as a principal component, i.e., the transparent conductive base material concerning an example 6, was obtained.

[0055] And the film property of the transperence two-layer film formed on the glass substrate is shown in the following table 1. Moreover, the reflective profile of the transparent conductive base material concerning the manufactured example 6 is shown in drawing 9 , and a transparency profile is shown in drawing 10 .

[0056] The colloidal dispersion liquid of a silver particle prepared by the same approach as the [example 7] example 1 is used. 0.4g of hydrazine water solutions and an auric acid potassium water solution (Au:0.075%) are used 1%. Obtain the distributed concentration liquid of a noble-metals coat silver particle, and the solution which contained the tetramer (trade name methyl silicate 51 by the COL coat company) of the tetramethyl silicate as an inorganic binder in this is added. the coating liquid for transperence conductive layer formation (Ag: -- 0.29%) which the noble-metals coat silver particle with a mean particle diameter of 7.0nm distributed Au: 0.052%, SiO₂ : 0.02%, water : [8.78%, EA:85.85%,] While DAA:5.0% is obtained and weight average molecular weight uses the glass substrate which diluted so that SiO₂ (silicon oxide) solid-content concentration might become 0.7% using the silica sol liquid of 2460, and was heated by 35 more degrees C Except having carried out the spin coat of the

coating liquid for transparence conductive layer formation, and the silica sol liquid the condition for 60 seconds by 150rpm, and having stiffened 210 degrees C for 20 minutes It carried out like the example 1 and the glass substrate with the transparence two-layer film which consisted of a transparence conductive layer containing a noble-metals coat silver particle and a transparence coat layer which consists of the silicate film which uses silicon oxide as a principal component, i.e., the transparent conductive base material concerning an example 7, was obtained.

[0057] The film property of the transparence two-layer film formed on the glass substrate is shown in the following table 1.

[0058] After adding 39g of iron(II) sulfate water solutions, and the mixed liquor of 48g of 37.5% sodium-citrate water solutions to 33g of silver-nitrate water solutions 23% [example 8] 9% and filtering and washing sediment, pure water was added and the colloidal dispersion liquid (Ag:0.49%) of a silver particle was prepared. Having added 5g of 1% water solutions of hydrazine 1 hydrate (N_2H_4 and H_2O), and stirring in 240g of colloidal dispersion liquid of this silver particle, 200g (Pt:0.06%) of platinum (IV) acid potassium $[K_2Pt(OH)_6]$ water solutions was added, and the colloidal dispersion liquid of a noble-metals coat silver particle with which coating of the platinum simple substance was carried out was obtained. After condensing the colloidal dispersion liquid of this noble-metals coat silver particle with an ultrafiltration, ethanol (EA) and diacetone alcohol (DAA) were added to the desalted concentration liquid which repeated and acquired the process which adds pure water to this concentration liquid, and is again condensed with an ultrafiltration, and the coating liquid for transparence conductive layer formation (Ag:0.245%, Pt:0.025%, water: 7.48%, EA:87.25%, DAA:5.0%) was obtained. As a result of observing the obtained coating liquid for transparence conductive layer formation with a transmission electron microscope, the mean particle diameter of a noble-metals coat silver particle was 9.2nm.

[0059] This coating liquid for transparence conductive layer formation next, on the glass substrate (soda lime glass with a thickness of 3mm) heated by 40 degrees C The transparence conductive layer which carries out the spin coat (for 130rpm and 60 seconds) of the silica sol liquid, is made to harden 180 degrees C for 20 minutes further continuously, and contains a noble-metals coat silver particle after carrying out a spin coat (for 130rpm and 60 seconds), The glass substrate with the transparence two-layer film which consisted of transparence coat layers which consist of the silicate film which uses silicon oxide as a principal component, i.e., the transparent conductive base material concerning an example 8, was obtained.

[0060] The above-mentioned silica sol liquid methyl silicate 51 (trade name by the COL coat company) here The 19.6 sections, The ethanol 57.8 section, the 1% nitric-acid water-solution 7.9 section, and the pure-water 14.7 section are used. SiO_2 That whose solid content (silicon oxide) concentration is 10% is prepared, and it is SiO_2 eventually. It diluted with the mixture (IPA/NBA=3/1) of isopropyl alcohol (IPA) and n-butanol (NBA), and has obtained so that solid content concentration may become 0.65%.

[0061] And the film property of the transparence two-layer film formed on the glass substrate is shown in the following table 1. Moreover, the reflective profile of the transparent conductive base material concerning the manufactured example 8 is doubled with drawing 11 and drawing 13, and a transparency profile is doubled with drawing 12 and drawing 14, and it is shown.

[0062] The colloidal dispersion liquid of a silver particle prepared by the same approach as the [example 9] example 8 is used. 6.3g of and 1% water solutions of hydrazine 1 hydrate (N_2H_4 and H_2O), The mixed solution of 121g (Au:0.098%) of water solutions and 121g (Pt:0.065%) of aurate $[KAu(OH)_4]$ potassium [platonic acid] $[K_2Pt(OH)_6]$ water solutions is used. the coating liquid for transparence conductive layer formation (Ag: -- 0.26%) with which the complex of gold and platinum distributed the noble-metals coat silver particle with a mean particle diameter of 11.7nm by which coating was carried out Au: 0.03%, Pt:0.02%, water : except having obtained 7.48%, EA:87.2%, and DAA:5.0% It carried out like the example 8 and the glass substrate with the transparence two-layer film which consisted of a transparence conductive layer containing a noble-metals coat silver particle and a transparence coat layer which consists of the silicate film which uses silicon oxide as a principal component, i.e., the transparent conductive base material concerning an example 9, was obtained.

[0063] And the film property of the transparence two-layer film formed on the glass substrate is shown in the following table 1. Moreover, the reflective profile of the transparent conductive base material concerning the manufactured example 9 is shown in drawing 15 , and a transparency profile is shown in drawing 16 .

[0064] Agitating using the colloidal dispersion liquid of a silver particle prepared by the same approach as the [example 10] example 8 without adding the above-mentioned hydrazine water solution as a reducing agent 203g (Pt:0.064%) of platinic acid potassium [K₂Pt (OH)₆] water solutions is added. By the substitution reaction of platinum and silver the coating liquid for transparence conductive layer formation (Ag: -- 0.24%) with which platinum distributed the noble-metals coat silver particle with a mean particle diameter of 9.2nm by which coating was carried out Pt: 0.025%, water : except having obtained 9.2%, EA:85.53%, and DAA:5.0% It carried out like the example 8 and the glass substrate with the transparence two-layer film which consisted of a transparence conductive layer containing a noble-metals coat silver particle and a transparence coat layer which consists of the silicate film which uses silicon oxide as a principal component, i.e., the transparent conductive base material concerning an example 10, was obtained.

[0065] The film property of the transparence two-layer film formed on the glass substrate is shown in the following table 1.

[0066] Agitating using 240g (Ag:0.49%) of colloidal dispersion liquid of a silver particle prepared by the same approach as the [example 11] example 8 without adding the above-mentioned hydrazine water solution as a reducing agent 203g (Pt:0.064%) of platinic acid potassium [K₂Pt (OH)₆] water solutions was added, and the solution which distributed the noble-metals coat silver particle with a mean particle diameter of 9.2nm to which coating of the platinum was carried out by the substitution reaction of platinum and silver was obtained. next, the inside of this solution -- the indium stannic acid ghost (ITO) particle (the Sumitomo Metal Mining Co., Ltd. make --) of 0.03 micrometers of mean diameters The ITO dispersion liquid which fully desalted according to the ion exchange and were obtained, using trade name SUFP-HX are added. the coating liquid for transparence conductive layer formation (Ag: -- 0.312%) which the above-mentioned noble-metals coat silver particle and the ITO particle distributed eventually Pt: 0.0325%, ITO:0.12%, water : 12.3% and EA:87.23% are obtained. And weight average molecular weight uses the silica sol liquid of 1920, and it is SiO₂. While using the glass substrate which diluted so that solid content (silicon oxide) concentration might become 0.8%, and was heated by 35 more degrees C Except having carried out the spin coat of the coating liquid for transparence conductive layer formation, and the silica sol liquid the condition for 60 seconds by 150rpm, and having stiffened 210 degrees C for 20 minutes It carried out like the example 8 and the glass substrate with the transparence two-layer film which consisted of a transparence conductive layer containing a noble-metals coat silver particle and an ITO particle and a transparence coat layer which consists of the silicate film which uses silicon oxide as a principal component, i.e., the transparent conductive base material concerning an example 11, was obtained.

[0067] And the film property of the transparence two-layer film formed on the glass substrate is shown in the following table 1. Moreover, the reflective profile of the transparent conductive base material concerning the manufactured example 11 is shown in drawing 17, and a transparency profile is shown in drawing 18 .

[0068] The colloidal dispersion liquid of a silver particle prepared by the same approach as the [example 1 of comparison] example 1 is used. the coating liquid for transparence conductive layer formation (Ag: -- 0.3%) which the silver particle with a mean particle diameter of 6.9nm distributed, without carrying out golden coating Water : except having obtained 4.0%, EA:90.7%, and DAA:5.0% It carried out like the example 1 and the transparent conductive base material concerning a glass substrate 1, i.e., the example of a comparison, with the transparence two-layer film which consisted of a transparence conductive layer containing a silver particle and a transparence coat layer which consists of the silicate film which uses silicon oxide as a principal component was obtained.

[0069] And the film property of the transparence two-layer film formed on the glass substrate is shown in the following table 1. Moreover, the reflective profile of the transparent conductive base material

concerning the manufactured example 1 of a comparison is shown in drawing 1 and drawing 11, and a transparency profile is shown in drawing 2 and drawing 12.

[0070] the coating liquid for transperence conductive layer formation (the Sumitomo Metal Mining Co., Ltd. make --) with which the ITO particle with a [example 2 of comparison] mean particle diameter of 30nm was distributed by the solvent Trade name solvent deasphalting-104 and ITO:2% on the glass substrate (soda lime glass with a thickness of 3mm) heated by 40 degrees C After carrying out a spin coat (for 150rpm and 60 seconds), it is SiO₂ continuously. The spin coat (for 150rpm and 60 seconds) of the silica sol liquid diluted so that solid content (silicon oxide) concentration might become 1.0% is carried out. Furthermore, it was made to harden for 30 minutes and 180 degrees C of transparent conductive base materials concerning a glass substrate 2, i.e., the example of a comparison, with the transperence two-layer film which consisted of a transperence conductive layer containing an ITO particle and a transperence coat layer which consists of the silicate film which uses silicon oxide as a principal component were obtained.

[0071] And the film property of the transperence two-layer film formed on the glass substrate is shown in the following table 1. Moreover, the reflective profile of the transparent conductive base material concerning the manufactured example 2 of a comparison is shown in drawing 1.

[0072]

[A table 1]

	微 粒 子 の 種 類	貴金属のコーテ ィング量(注1)	表面抵抗 (Ω/\square)	可視光線 透過率(%)	透過率の標準 偏差 (注2)	ヘーズ 値(%)	ボトム反射率(%) ／ボトム波長(nm)
実施例1	Ag-Au	26.0重量部	490	72.7	3.29	0	0.1/515
実施例2	Ag-Au	35.6重量部	390	69.4	2.00	0.1	0.05/495
実施例3	Ag-Au	11.7重量部	395	72.5	2.72	0.1	0.08/505
実施例4	Ag-Au	10.2重量部	473	73.1	4.89	0	0.08/510
実施例5	Ag-Au + ITO	18.7重量部	456	74.8	3.01	0.4	0.46/540
実施例6	Ag-Au + ATO	16.6重量部	534	74.2	3.04	0.2	0.61/530
実施例7	Ag-Au	17.9重量部	313	71.2	2.40	0	0.02/465
実施例8	Ag-Pt	10.2重量部	658	71.6	2.91	0	0.07/525
実施例9	Ag-Au-Pt	19.2重量部	553	70.4	2.48	0.1	0.08/510
実施例10	Ag-Pt	10.4重量部	728	70.0	2.35	0.1	0.07/525
実施例11	Ag-Pt + ITO	10.4重量部	457	69.7	1.75	0.4	0.15/570
比較例1	Ag	—	980	70.9	6.67	0.1	0.23/485
比較例2	ITO	—	16000	93.3	—	0.2	0.83/540

注1：銀100重量部に対する金若しくは白金単体または金、白金複合体（貴金属）のコーティング量である。

注2：可視光線波長域（380～780nm）の5nmおきの各波長における透明基板を含まない透明2層膜だけの透過率（%）に対する値である。

[0073] The surface-electrical-resistance value of the transperence two-layer film which was immersed in brine 5% and formed the transparent conductive base material concerning the "weathering test" examples 1-11 and the transparent conductive base material concerning the example 1 of a comparison on the transperence substrate (glass substrate), and the membranous appearance were investigated. This result is shown in the following table 2.

[0074]

[A table 2]

	表 面 抵 抗 (Ω/\square)		2層膜外観 (透過率、ヘーズ値、反射)
	初期値	5%食塩水浸漬後の値	
実施例1	490	24時間浸漬で、表面抵抗値変化なし。	24時間浸漬で、透過率、ヘーズ値、及び、反射プロファイル変化なし。
実施例2	390	24時間浸漬で、表面抵抗値変化なし。	24時間浸漬で、透過率、ヘーズ値、及び、反射プロファイル変化なし。
実施例3	395	3時間浸漬で、表面抵抗値変化なし。24時間浸漬で、表面抵抗値3.1k Ω/\square に変化	1時間浸漬で、透過率、ヘーズ値、及び反射プロファイル変化なし。24時間浸漬で、反射色が若干変化。
実施例4	473	3時間浸漬で、表面抵抗値変化なし。24時間浸漬で、表面抵抗値620 Ω/\square に変化。	1時間浸漬で、透過率、ヘーズ値、及び反射プロファイル変化なし。24時間浸漬で、反射色が若干変化。
実施例5	456	24時間浸漬で、表面抵抗値変化なし。	24時間浸漬で、透過率、ヘーズ値、及び、反射プロファイル変化なし。
実施例6	534	24時間浸漬で、表面抵抗値変化なし。	24時間浸漬で、透過率、ヘーズ値、及び、反射プロファイル変化なし。
実施例7	313	24時間浸漬で、表面抵抗値変化なし。	24時間浸漬で、透過率、ヘーズ値、及び、反射プロファイル変化なし。
実施例8	658	6時間浸漬で、表面抵抗値変化なし。24時間浸漬で、表面抵抗値755 Ω/\square に変化。	6時間浸漬で、透過率、ヘーズ値、及び反射プロファイル変化なし。24時間浸漬で、反射色が若干変化。
実施例9	553	24時間浸漬で、表面抵抗値変化なし。	24時間浸漬で、透過率、ヘーズ値、及び、反射プロファイル変化なし。
実施例10	728	6時間浸漬で、表面抵抗値変化なし。24時間浸漬で、表面抵抗値1031 Ω/\square に変化	6時間浸漬で、透過率、ヘーズ値、及び反射プロファイル変化なし。24時間浸漬で、反射色が若干変化。
実施例11	457	24時間浸漬で、表面抵抗値変化なし。	24時間浸漬で、透過率、ヘーズ値、及び、反射プロファイル変化なし。
比較例1	980	15分浸漬で表面抵抗値、 $>10^6 \Omega/\square$ で測定不可に。	30分浸漬でヘーズ値上昇。10時間浸漬で、透明2層膜の一部が剥離する。

[0075] "Criticism **"

(1) It is checked that the value of the surface electrical resistance (Ω/\square) of the transparency two-layer film concerning each example and the standard deviation of permeability is remarkably improved compared with the value of the transparency two-layer film concerning each example of a comparison so that clearly from the result shown in a table 1. Moreover, in the transparent conductive base material of an example 1 and an example 8, it is also checked that the very flat transparency profile is obtained so that clearly from the comparison of the transparency profile of the transparent conductive base material concerning the example 1 and example 8 which were shown in drawing 2 and drawing 12, and the transparency profile of the transparent conductive base material concerning the example 1 of a

comparison. Moreover, in the transparent conductive base material applied to an example 1 and an example 8 compared with the examples 1 and 2 of a comparison, it is checked that the reflection property in a visible-ray wavelength region is also improved so that clearly from the reflective profile of drawing 1 and drawing 11.

(2) Moreover, it is checked that the weatherability of the transparence two-layer film applied to each example compared with the transparence two-layer film concerning the example 1 of a comparison is also improved remarkably so that clearly from the result shown in a table 2.

(3) Next, when a golden simple substance compares the visible-ray permeability of the transparent conductive base material concerning the examples 1-7 which have applied the noble-metals coat silver particle by which coating was carried out, the visible-ray permeability of the example 5 in which ITO was included so that it might be checked from a table 1, and the example 6 in which ATO was included shows the high value compared with other examples.

[0076] On the other hand, when a platinum simple substance or gold, and platinum complex compare the surface electrical resistance of the transparent conductive base material concerning the examples 8-11 which have applied the noble-metals coat silver particle by which coating was carried out, the surface electrical resistance of the example 11 in which ITO was included is the smallest value so that it may be checked from a table 1, and it has become the value of abbreviation identitas about visible-ray permeability, respectively. namely, the example 11 -- the surface-electrical-resistance value of examples 8-10, and abbreviation -- when the thickness of a transparence conductive layer is more thinly set up so that it may become the same, it is shown that the visible-ray permeability of a transparence conductive layer can be made higher than examples 8-10.

[0077] When conductive oxide particles, such as ITO and ATO, are included in a transparence conductive layer from this etc., it is checked that improvement in the film permeability in a transparence conductive layer can be aimed at.

(4) In addition, although the noble-metals coat silver particle is prepared as the above-mentioned aurate and platinate in examples 1-11 with the application of an auric acid potassium and a platinic acid potassium, the experiment which replaced with auric acid potassiums, such as this, and a platinic acid potassium, and applied auric acid sodium and platinic acid sodium is also conducted.

[0078] And it is checking that perform the assessment trial same also about the noble-metals coat silver particle obtained with the application of auric acid sodium and platinic acid sodium as examples 1-11, and the same assessment is obtained.

[0079]

[Effect of the Invention] Since the transparence conductive layer which constitutes one side of the transparence two-layer film is using as the principal component the noble-metals coat silver particle of 1-100nm of mean diameters and binder matrix which coated the front face with gold, a platinum simple substance, or the complex of gold and platinum according to the transparent conductive base material concerning invention according to claim 1 to 6, it has the acid-resisting effectiveness and the transmitted-light profile which were excellent compared with the conventional transparent conductive base material, and has good weatherability and conductivity.

[0080] Moreover, since according to the manufacture approach of the transparent conductive base material concerning invention according to claim 7 to 12 it is heat-treating after applying the coating liquid which uses as a principal component a noble-metals coat silver particle with a mean particle diameter of 1-100nm distributed by a solvent and this solvent on a transparence substrate and applying the coating liquid for transparence coat stratification subsequently, it has the effectiveness that it is low cost and the transparent conductive base material concerning claims 1-6 can be manufactured simple.

[0081] Furthermore, according to the display concerning invention according to claim 13, since a transparent conductive base material according to claim 1 to 6 carries out the transparence two-layer film side outside and is incorporated as a front plate, a surface echo of the display screen is controlled and the high electric-field shielding effect is provided.

[Translation done.]